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Pulse Laser Assisted Composite Electroless Deposit to Prepare Ceramic Coating

Qunli Zhang[a,b,c], Jianhua Yao[b,c], Yi Pan[a,*]

[a]Department of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, China
[b]Key Laboratory of Special Purpose Equipment and Advanced Processing Technology, Ministry of Education, Hangzhou, 310014, P. R. China
[c]Research Center of Laser Processing Technology and Engineering, Zhejiang University of Technology, Hangzhou, 310014, P. R. China

Abstract

The Ni-P-nano Al_2O_3 plating layer was prepared on 45 steel by composite electroless deposit, and then hardened by pulse Nd:YAG laser. The surface morphology, microstructure, phase composition, and hardness were investigated respectively. The results show that there is a firm metallurgical bonding between the treated layer and the substrate. Hard phases such as Al_5FeNi, FeNi and $Fe_{0.64}Ni_{0.36}$ form on the surface of composite electroless deposit layer after laser treatment, which contributes to the hardening of coating through fine-crystal strengthening and dispersion strengthening. The hardness of laser treated layer is 4.5 times higher than that of the substrate.

Keywords: Ni-P electroless plating; nano Al_2O_3 ; laser; microstructure; property

1. Introduction

Different from conventional electroless plating, composite electroless plating is realized by adding insoluble solid particles such as oxides and carbides into plating solution to fulfill metal and particle co-deposition. Following the co-deposition, a suitable heat treatment is necessary to transform the amorphous structures in the plated layer to crystalline to enhance the deposit layer properties. Due to simpleness and high efficiency, composite electroless plating is applied extensively in industry. However, traditional heat treatment techniques usually need long time duration at high temperature, which causes sample deformation and base materials degradation. Therefore, composite electroless plating with conventional treatment processing is not suit for the components which need high dimensional precision and strength.

Laser hardening technology has been used to replace conventional heat treatment after composite electroless plating. The laser hardening was performed by laser beam scanning over the electroless plated surface. Because of locally fast heating and cooling, the laser hardening treatment will cause neither serious distortion nor base materials

* Corresponding author. Tel.: +86-571-87953008; fax: +86-571-87953008.
E-mail address: zql@zjut.edu.cn.

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degradation, thus keeping high precision and strength of the samples. The laser hardening treatment is believed to be an effective treatment method after composite electroless plating. Razavi prepared the hardened layer of Ni-Al intermetallic compound by laser treated Ni-P plating on Al356 substrate [1]. Yang et al. investigated that the amorphous Ni-P coating on aluminum formed by electroless plating was transformed to Ni and Ni_3P precipitates under YAG pulse laser irradiation and heat treatment above 300 °C for 2.5 h [2,3].

As a kind of cheap abrasive material with high hardness and excellent chemical stability, Al_2O_3 is believed to be an effective oxide to co-deposit with Ni-P coating together. Because of excellent properties of nanometer material [4,5], nanometer Al_2O_3 has been investigated and applied widely. Zheng Xiaohua and Dun Aihuan et al. studied the microstructure of Ni-P-Al_2O_3 electroless composite plating on Fe-C alloy treated by continuous CO_2 laser beam [6,7], and came to the conclusions that the bonding force between the electroless plating and the substrate was increased by laser processing and the properties of plating layer were greatly improved.

However, most researches mentioned above focus on the deposition on Al alloy or with heat source of continuous CO_2 laser. CO_2 laser and Nd:YAG laser are thought as the main sources to perform laser processing. Because of high power and large beam size of CO_2 laser, most of the coatings were obtained by using CO_2 laser. However, the continuous CO_2 laser is limited in precision cladding because CO_2 laser is prone to cause overheating and distortion. Pulse Nd:YAG laser is especially suitable for precision cladding on local region of steel, due to its high single pulse energy, various changeable parameters, short wavelength and flexible processing [8].

In this paper, pulse Nd:YAG laser was tried to irradiate Ni-P-nano Al_2O_3 composite electroless deposit on 45 steel, the microstructure and hardness of composite electroless plating layer were analyzed and the hardening mechanism of nano Al_2O_3 was investigated.

2. Experimental Procedures

45 steel after modified treatment with hardness of $HV_{0.2}180$ was used as the base material, with the chemical composition shown in Table 1. The dimension of the specimen was 50×30×2 mm^3. The substrate sample was polished, cleaned and dried as the pretreating steps. Al_2O_3 powder with average grain size (APS) of 20nm used as the insoluble component in the composite electroless suspension was pretreated with chemically deoiling with lye and cleaning with cold water. After component optimization, the nano-Al_2O_3 powder was added into the Ni-P electroless bath, and stirred by ultrasonic treatment for above 60min to achieve homogeneous suspension. Then the compound electroless plating with depth of 0.02mm was achieved, the surface microhardness of which is $HV_{0.2}525$.

The laser heating experiments were performed by a pulse wave Nd:YAG laser system with a rated power of 300W and with a low order mode. The beam with diameter of 3mm was used after a lens with focal length of 75mm, and argon was used as shielding gas to protect the nano-particles from burning lost. The laser beam power and scanning speed were adjusted during the experiments to achieve the cladding layer with different parameters. Finally, the current of 250A, pulse width of 2.5ms, pulse frequency of 20Hz and overlapping ratio between adjacent tracks of 66% were set as the optimized laser parameters.

Transverse sections of deposition layers were cut, mechanical polished and etched by ethanol solution of 4% HNO_3 for microstructural studies. Phase identification of Ni-P-Al_2O_3 composite coating was performed by X-ray diffraction (XRD, Thermoarl-SCINTAGX’ TRAX). The element distribution was analyzed by X-ray energy dispersion spectrometer (EDS, Hitachi S-4700). The Vickers hardness of the sample was measured on HXD-1000 hardness instrument under a load of 200g with a dwelling time of 15s. The hardnesses of three points in same region were tested and the average value was treated as the final hardness.

Table 1. Chemical composition of 45 steel (wt. %)

C	Si	Mn	P	S	Fe
0.43	0.23	0.66	0.002	0.014	Bal.

3. Results and discussion

3.1. Surface morphology of as-plated coating

Fig.1(a) shows the morphology of Ni-P-Al_2O_3 electroless deposit layer. It can be seen that cellular cells with size of 10μm are populated over the surface of electroless plating. After adding nano-Al_2O_3 into the plating bath, the cellular structure of the plated layer forms in the mode of heterogeneous nucleation and grows during deposition. The random distribution of the cellular cells forms the smooth composite layer with high density, with hardness of $HV_{0.2}$350. According to the former researches [9,10], when the phosphorus composition is more than 8% in Ni-P electroless plating, the structure of coated surface were amorphous rather than crystalline. In this paper, the content of phosphorus is 9.3% determined through EDS analysis. Fig.1(b) shows the XRD spectrum of as-plated Ni-P-Al_2O_3 coating. A wide peak appears at 2θ =45°, which shows the typical diffraction peak of amorphous material. It can be seen that after adding nano-Al_2O_3 into Ni-P electroless solution, the compound material is still amorphous.

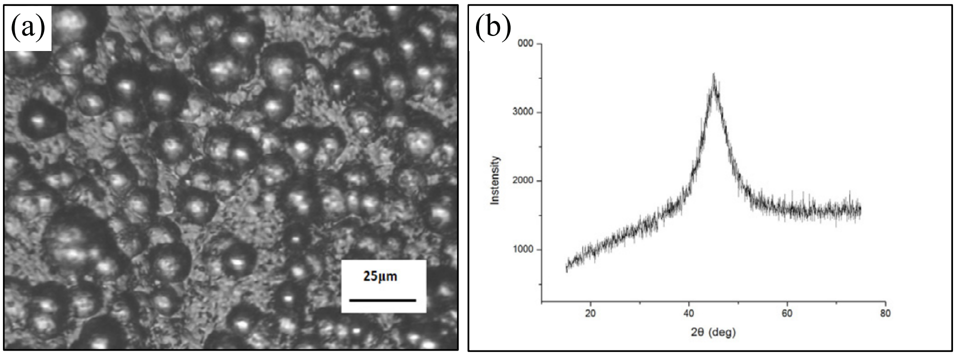

Fig. 1. (a) Morphology of as-plated Ni-P- Al_2O_3 coating; (b) the corresponding XRD pattern of as-plated coating

3.2. Microstructure and phases of hardened layer

When pulse laser was introduced on the Ni-P-Al_2O_3 electroless coating, the surface of material went through four stages, heating, melting, crystallizing and solidifying. The surface morphology of as-plated coating after laser treatment is shown in Fig.2 (a). Compared with the morphology of as-plated coating (Fig.1), the cellular cells disappear and the surface is smoother with thinner grains. It indicates that the coating layer smelted and solidified newly after irradiated by laser beam. Fig.2 (b) is the top region of the cross section of hardening coating. Because the cooling rate of the molten pool surface is the fastest, the microcrystallite structures formed in the region 18μm below the surface. The magnified SEM image of the microcrystallite structures is shown in Fig.2 (c). It can be seen that the structures mainly consist of tiny and stagger quadric dendrites, and the tiny cellular structures with size of 1-3μm caused by intersecting of the quadric dendrites. Several white particles with uniform distribution were observed in hardened layer. Fig.2 (d) shows the high magnified image of the white particles, which have the diameter of 300nm and exist both on grain boundary and in crystal grain. The element component of white particles was analyzed by EDS, which is shown in Table 2 and Fig.3. The results illustrate that the particle is consisted of Al, Fe and Ni elements. Pt element also exists in laser treated layer, the reason for which is speculated that the spraying of Pt on the sample surface for increasing its conductivity. The white particles can prevent the growth of grains and promote the transformation of fine grains. At the same time, as the heterogeneous nucleation, the white particles contribute to the increment of melt nucleation rate.

To investigate the phases of the laser treated coating, XRD analysis was performed, which is shown in Fig.4. It can be seen that Al_5FeNi, FeNi and $Fe_{0.64}Ni_{0.36}$ form in the composite electroless deposit layer after laser treatment.

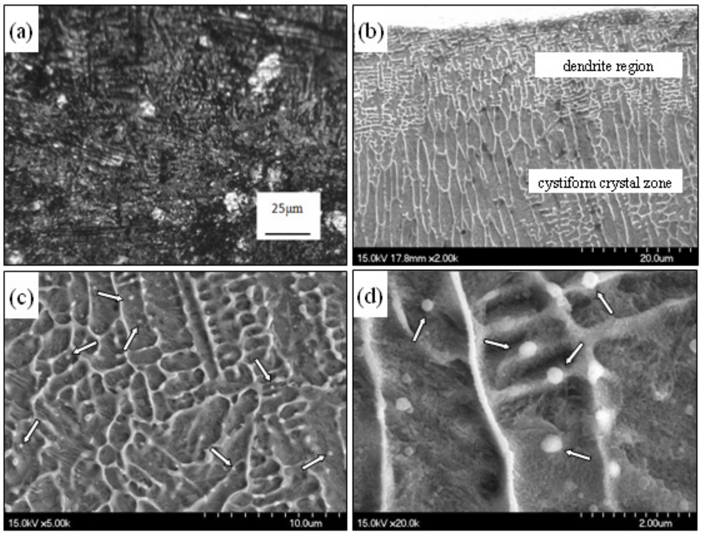

Fig. 2. (a) The surface morphology; (b) The top and central microstructure of hardened layer; (c) The dendrite region in the top of hardened layer; (d) Particles in dendrite region

Because of the special chemical property of nanometer Al_2O_3, Al_2O_3 particles decomposed at high temperature caused by the irradiation of high energy laser beam, reacted with Fe and Ni elements, and then form Al_5FeNi.

In the middle part of laser treated plating layer (Fig.5), it can be seen that the structures are composed of cellular crystals and few cellular dendrites. The grains in this region are obviously larger than that of top part, which is caused by solidification rate reduction along with the depth of coating. Fig.6 shows the structure of the bottom part of plating layer and the fusion area. The columnar crystals along the vertical direction of the laser scanning and few cellular dendrites in the bottom part of plating layer can be seen.

Table 2. Element atomic percentage of white particles in Fig.2 (d)

Elements	Al	Fe	Ni	Pt
Atom %	0.19	82.57	8.78	8.46

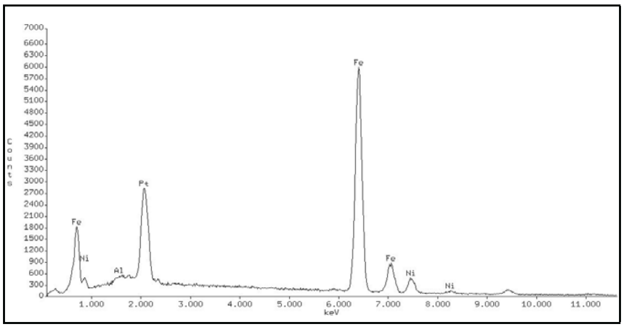

Fig. 3. EDS pattern of white particles in Fig.2 (d)

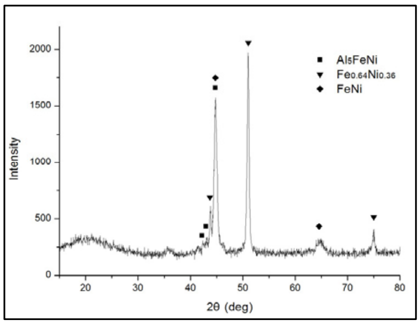

Fig. 4. XRD pattern of strengthened layer

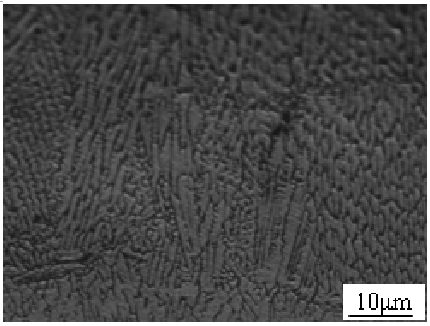

Fig. 5. Microstructure on middle part of laser treated layer

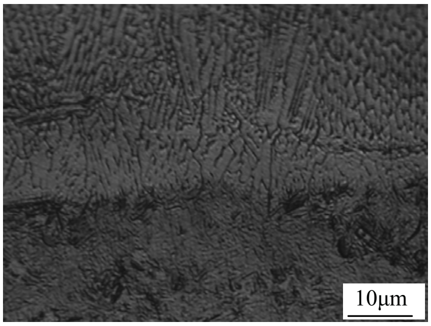

Fig. 6. Microstructure on bottom of laser treated layer

The laser energy not only affects the Ni-P-Al_2O_3 electroless coating, but also transfers to the bonding region and the substrate, which forms the heat affected zone. It can be seen that the needle-like martensites with small size form in the fusion area. There is firm metallurgical bonding between the laser treated coating and the substrate, which is quite different from the mechanical bonding by using traditional spray and electroless plating.

3.3. Microhardness analysis

Fig.7 shows the curves of microhardness against depth of strengthened layer for both as-plated and the laser treated Ni-P-Al_2O_3 electroless coating. The hardness of the coating surface without laser treatment is $HV_{0.2}$490, but that of the coating surface with laser treatment is $HV_{0.2}$587. The hardness reduces to $HV_{0.2}$520 on the layer 25μm below surface, which can be interpreted by two reasons. One is the particle size. From Fig.3, the grain size on the surface of plating layer is about 1μm, while that of grains in the sub-surface layer is 2-3μm. Finer the grains is, higher the microhardness would be. The other reason is the specific phase distribution. The hard phase Al_5FeNi, FeNi and $Fe_{0.64}Ni_{0.36}$ form on the surface of composite electroless deposit layer after laser treatment, which contributes to the hardening of the coating through fine-crystal strengthening and dispersion strengthening.

However, the highest hardness of $HV_{0.2}$840 occurs in the fusion zone, about 80μm below the surface, which is 1.7 times that of as-plated Ni-P-Al_2O_3 electroless coating and 4.5 times of the substrate. With inserting of high energy laser beam into the Ni-P-Al_2O_3 electroless coating, Ni and P elements diffuse into the substrate and form the fusion zone. Phosphides distribute in this region uniformly, which contributes to the hardness. Because of the short pulse width and high cooling rate of the pulse YAG laser, the diffusion is limited, and then the thickness of fusion zone is only 15-18μm. Below the fusion zone, the heat affected zone consisting of needle martensites forms. Due to the high degree of supercooling, the size of martensite is quite thin, which results in phase transformation hardening and thin grains hardening.

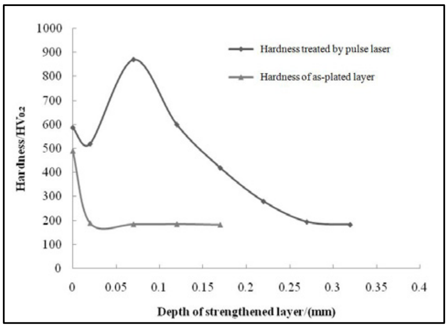

Fig. 7. The microhardness comparison between as-plated layer and laser treated layer

4. Conclusions

- The pulse Nd:YAG laser treatment of the pre-prepared Ni-P-nano Al_2O_3 electroless co-deposit layer on 45 steel can be successfully performed and the structure and hardness of the plated layer can be improved by the laser treatment.
- The compound material is still amorphous after adding nano-Al_2O_3 into Ni-P electroless solution before laser irradiation. The Ni-P-nano Al_2O_3 electroless coating went through heating, melting, crystallizing and solidifying under high energy laser casting, which forms a firm metallurgical bonding between the treated layer and the substrate.
- Hard phase Al_5FeNi , as well as intermetallic compounds such as FeNi and $Fe_{0.64}Ni_{0.36}$ form on the surface of composite electroless deposit layer after laser treatment, which contributes to the hardening of the coating through fine-crystal strengthening and dispersion strengthening.
- The highest hardness with $HV_{0.2}840$ occurs in the fusion zone, which is 1.7 times that of as-plated Ni-P- Al_2O_3 electroless coating and 4.5 times of the substrate. It is the phosphides in fusion zone distributing uniformly and diffusely that contribute to increasing of the microhardness.

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